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STUDIES OF ELECTRON-BEAM-INDUCED DECOMPOSITION OF BENZENE

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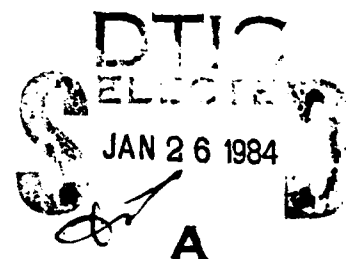
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Experiments have been performed using a Febetron 706 electron beam to study the problems that may occur when benzene is introduced into an electron accelerator. We particularly address the problem of electron-induced fragmentation and polymerization into nonvolatile species that deposit on surfaces, leading to the possibility of surface breakdown in accelerating gaps.		

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20. ABSTRACT (Continued)

Our results show that the amounts of fragmentation and deposition are quite small for a finite number of e-beam pulses, but that problems could arise after extended periods of use. As a conservative design guideline, we estimate that the fragmentation cross section for high energy electrons on benzene is approximately 10^{-16} cm^2 and that 10% of these collisions lead to surface deposits.

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FIGURES

1. Schematic of Experimental Setup
2. Infrared Absorption Spectrum of Surface Deposits

TABLE

1. Test Conditions for Benzene Decomposition Study

I INTRODUCTION

Past and current experiments on the experimental test accelerator (ETA) facility at Lawrence Livermore National Laboratory (LLNL) are showing the efficacy of beam conditioning by laser-assisted ion-focus regime (IFR) propagation.¹ In these experiments, a low pressure of gas (0.1-10 μm) is introduced into the propagation region. The gas is chosen to be one that can be easily photoionized; experiments to date use benzene (C_6H_6), which has a large two-photon photoionization cross section at 248 nm. The photoionization driver is a KrF laser. Operationally, the laser is pulsed shortly before the e-beam is fired, causing preionization of a channel in the propagation region. The radial electric field in the nose of the electron beam expels the slow moving photoelectrons, leaving behind the positively charged ion column, which then exerts an electrostatic focusing force on the electron beam.

The magnitude of the two-photon ionization cross section of benzene at 248 nm is enhanced because the one-photon transition to an intermediate state is resonant with an allowed absorption. The intermediate real level is apparently a dissociating state, so excitation of benzene with 248 nm radiation leads to fragmentation,² presumably into lighter molecular weight, volatile species. However, black deposits have also been observed on windows where the laser beam enters the cell,^{1,3} indicating that polymerization and/or decomposition to a carbonaceous material takes place. The importance of surface catalysis in the latter process is not known.

In addition to the fragmentation induced by uv radiation, it might be anticipated that significant chemical reactions could be induced by high energy electrons. In either case, if carbonaceous material is deposited on the surfaces of the insulators in the accelerator gaps, it could lead to the buildup of a conducting layer that would cause surface breakdown across the gaps. In this study, we are addressing the problem of electron-beam-induced decomposition of benzene by performing chemical and optical

analyses of the residual gas and of surface deposits in a benzene-filled cell subjected to Febetron 706 e-beam pulses.

II EXPERIMENTS

A schematic of the experimental arrangement is shown in Figure 1. The aluminum cell (12-in. O.D. by 18-in. long) was thoroughly cleaned with acetone before each series of test shots. The cell was evacuated to 15 μ m pressure before filling with reagent-grade benzene. Liquid benzene was put in a stainless steel reservoir and was purified by three freeze-pump-thaw cycles before use.

In the first test series, the valve between the reservoir and the test cell was open during all the shots. In the second series, N_2 was used and the valve was closed. In the third and fourth series, the cell was filled to the room-temperature vapor pressure of benzene (55 ± 2 torr depending on T), and the valve was closed. Series 1 through 3 consisted of 100 Febetron pulses each, whereas series 4 was 250 shots. The test conditions are summarized in Table 1.

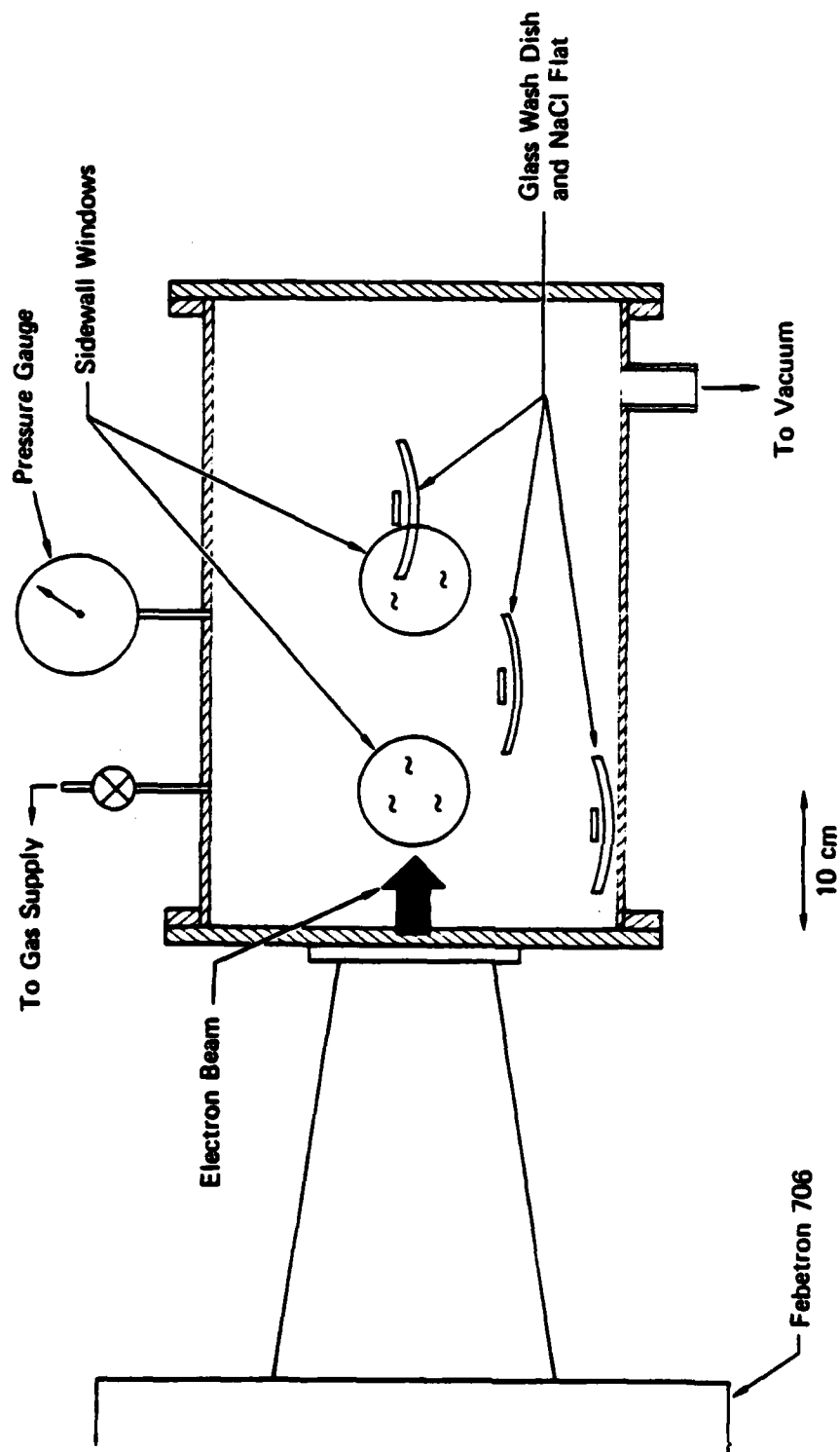
Table 1
TEST CONDITIONS FOR BENZENE DECOMPOSITION STUDY

<u>Series</u>	<u>Gas</u>	<u>P_{initial} (torr)</u>	<u>P_{final} (torr)</u>	<u>No. of Pulses</u>
1	Benzene	70	(a)	100
2	N_2	70	66	100
3	Benzene	57	54	100
4	Benzene	53	47	250

(a) Valve to reservoir open during test.

Test surfaces consisting of three NaCl flats and three glass wash dishes were placed in the cell in the positions shown in Figure 1. It was intended that gas-phase products of the electron-induced reactions would condense on these surfaces, but some electrons impinged directly on the surfaces (causing intense color-center formation and fracturing of the NaCl windows). We cannot distinguish between condensation products and products formed directly on the surface.

The Febetron 706 e-beam source used in these experiments produces a 3-ns pulse of 600 keV electrons with a total current of ~ 5000 A in a beam that is initially ~ 2 cm in diameter. The total charge is therefore ~ 15 μC /pulse. For comparison, ETA pulses are 6000 A for 20 ns, for a charge of ~ 120 μC /pulse. However, we used benzene pressures of about 50 torr, whereas the pressure in the ETA experiments is ≤ 1 μm . Thus, in terms of products formed, each Febetron pulse corresponds to approximately 6000 ETA pulses.



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FIGURE 1 EXPERIMENTAL ARRANGEMENT FOR BENZENE DISSOCIATION STUDIES

III RESULTS AND OBSERVATIONS

After the first series of 100 pulses into 70 torr of benzene, we observed a marked black deposit on the surfaces of the test cell nearest the e-beam source. The deposits were easily removed by wiping with Kimwipes wetted with acetone and were completely consistent with the decomposition of benzene. The cell surfaces farthest from the e-beam remained very clean. As a check on this observation, a series of 100 shots into N_2 was undertaken. In this test, all the surfaces remained clean. At that point, our fears about benzene decomposition seemed to be confirmed. However, after the third series of 100 shots into 57 torr of benzene and the fourth series of 250 shots into 53 torr of benzene, we did not observe the black deposits.

We can suggest two possible explanations for this anomaly. First, these experiments were the first time that the new test cell was used. Even though it was thoroughly cleaned with acetone before the tests, it is possible that some machining oils or other impurities remained on or in the surface and that electron bombardment led to the black surface deposits. The second (and more likely) possibility is that in the first test series the valve to the benzene reservoir was left open. This could have led to benzene condensation on the cell surfaces, and electron bombardment of the liquid could have led to carbon formation. In either case, we did not observe black deposits on the aluminum surfaces in the last two test series, which more closely represent ETA conditions.

To further characterize the surface deposits, we measured the transmission loss of various optical components in the cell. The cell was fitted with three Homosil windows mounted in flanges at the horizontal midplane (window surfaces vertical). These windows were not cleaned between the test series. At the completion of all tests, the transmission through all three windows in series was measured over the 400-700 nm range. The windows were then cleaned with acetone and the measurement was repeated. No change in transmission was found, indicating that no

absorbing material deposited on these vertical surfaces during the entire test sequence.

We performed the same sequence of transmission measurements on the three wash glasses that were placed horizontally in the cell (Figure 1) during the third series of tests (100 shots into benzene at 57 torr). In this case, we found that removable deposits caused a 15% reduction of transmission when the three glasses were measured in series. Thus, even though the aluminum surfaces appeared clean in that set of shots, measurable deposits were found on the wash glasses.

If we assume that each surface was coated with a deposit that absorbed 5% at 500 nm, we can use the optical constants for carbonaceous materials from Reference 4 to determine that each deposit was $\sim 0.0003 \mu\text{m}$ thick. Pure carbon has a density of $\sim 2 \text{ g/cm}^3$, so such a layer would weigh $6 \times 10^{-7} \text{ g/cm}^2$. This corresponds to the decomposition of 5×10^{15} benzene molecules for each cm^2 of surface coated. If we assume uniform deposition on the entire cell surface of 6000 cm^2 , the total decomposition would amount to 3×10^{19} molecules. Since the total number in the cell was approximately 6×10^{22} molecules, the assumed decomposition would amount to 0.05%. In terms of pressure, this would be 0.03 torr.

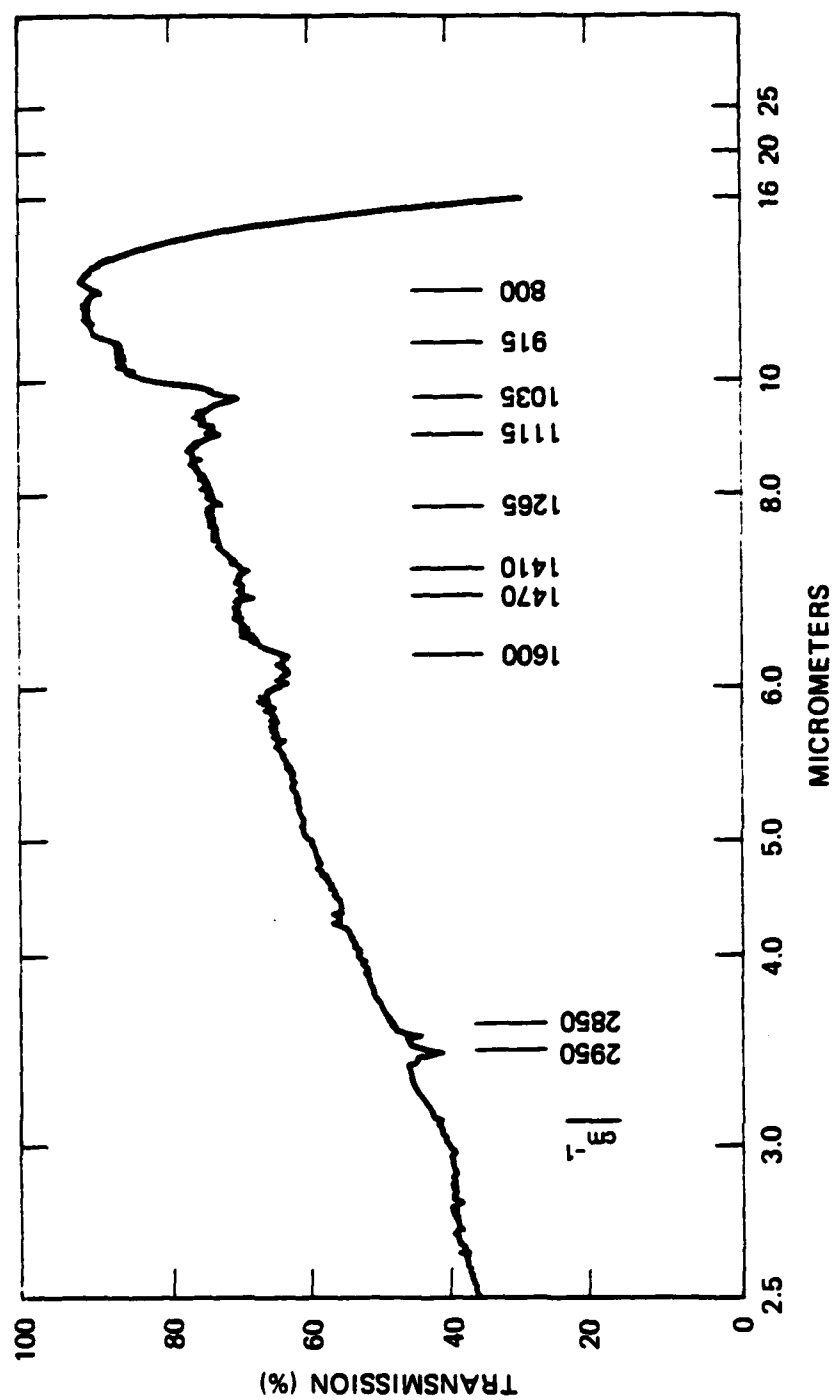
We measured the change in pressure during the tests, with the results shown in Table 1. For the third series, the change was 3 torr, or 100 times the amount required to account for the measured window absorption. The discrepancy could be due to the assumption that the window deposits are nearly pure carbon. The higher the hydrogen content, the lower the absorption coefficient.⁴ Thus the coefficient used to estimate the thickness of the deposit could be too large; i.e., the more polymeric the material, the thicker the deposit would have to be to produce the observed window absorption. Another possibility is that volatile polymers are formed that reduce the total number of molecules and thus the pressure. However, no real significance should be attached to the pressure change measurement since we also measured a 4-torr decrease in the N_2 test series, where no chemical changes should occur.

In an effort to identify the nature of the surface deposits, we measured the infrared absorption spectrum of the NaCl windows. Because the absorption features were quite weak, the spectra for the samples from individual windows showed only absorption at 2850 and 2940 cm^{-1} .

We then used the NaCl windows from the third test sequence (100 shots into 57 torr benzene) to measure the spectrum of the three windows in series. The results, shown in Figure 2, allow identification of additional absorption features in the 6 to 12 μm region. These absorption features are characteristic of aliphatic hydrocarbons, although even the enhanced spectrum of Figure 2 is not detailed enough to allow a more specific identification. Thus, the polymeric deposits have a different structure from the aromatic benzene.

In an attempt to obtain a denser sample of the deposit, we ran the fourth sequence of 250 shots into benzene at 53 torr. At the completion of the test, the entire surface of the cell was wiped with a swab of glass wool soaked in acetone. The swab was then washed with cyclohexane, and the resulting solution was drained into the cell holder of a freshly pressed KBr pellet. The solution was dried at 85°C for 1 hour, and the IR spectrum of the pellet plus residue was measured. Unfortunately, no absorption features were observed, and we can only speculate that the material observed as deposits in the previous tests evaporated at the elevated drying temperature used.

We also examined the gas-phase products of the electron-bombarded benzene by gas chromatography (GC). At the completion of the third sequence (100 shots into 57 torr benzene), samples of the residual gas were withdrawn by syringe from the cell and injected into the GC. Very small components of more volatile species were detected, but nothing less volatile than benzene could be observed. In all tests, the benzene peak constituted 97.9% to 99.5% of the total. Thus, if the detector sensitivity to different species is fairly uniform, we can conclude that there is small but measurable (~ 1%) residual fractionation of the benzene to lighter molecular weight stable species.



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FIGURE 2 INFRARED ABSORPTION SPECTRUM OF THREE NaCl FLATS EXPOSED TO E-BEAM-EXCITED BENZENE

IV DISCUSSION AND CONCLUSIONS

Our tests of 100 Febetron 706 shots into ~55 torr of benzene were equivalent in total charge times density of benzene to approximately 10^5 shots of ETA into 0.5 μm benzene (28 hours at 1 Hz). The present tests differ from the ETA case, however, because the Febetron beam is not collimated and so electrons strike the walls. We cannot distinguish between effects occurring in the gas-phase and those that occur on the surfaces.

On the basis of our observations, it would appear that the effects of the electron bombardment of benzene are relatively minor. The gas chromatography analysis indicates the presence of gas-phase products of about 1% decomposition, whereas the optical transmission measurements indicate that surface deposits could account for up to 0.05% decomposition. We will now show that these levels suggest that the fragmentation of benzene by electron collision, although small, is in fact consistent with expectations.

The total number of dissociation collisions per shot, C , can be written

$$C = \phi N \sigma L,$$

where ϕ is the electron flux per shot ($\sim 10^{14}$), N is the benzene density ($\sim 2 \times 10^{18}/\text{cm}^3$), σ is the dissociation cross section, and L is the electron path length. To take into account multiple scattering on the electron trajectories, we will assume that $L \approx 100$ cm, which is approximately twice the cell length.

We have not located data on values of σ for benzene, but McDaniel et al.⁵ report values for ethane (C_2H_6) for the energy range $15 \leq \epsilon \leq 600$ eV. The peak value is $7.6 \times 10^{-16} \text{ cm}^2$ at 80 eV. An extrapolation of these values to 600 KeV using the Born approximate ($\sigma \propto 1/E$) gives a predicted value of

$\sigma_{\text{dissociation}} \leq 10^{-18} \text{ cm}^2$. Using the above parameters for our experiments, we calculate $C = 2 \times 10^{16}$ fragments/shot, or 2×10^{18} per 100 shots. This corresponds to only 0.003% dissociation. Although the uncertainties in both our gas-phase and surface fragmentation measurements are large, it seems quite certain that the levels exceed the calculated value. Thus, we conclude that benzene is irreversibly fragmented by high energy electron impact with a cross section exceeding 10^{-18} cm^2 .

For design purposes, it is probably conservative to estimate that the dissociation cross section of benzene by high energy electrons is on the order of 10^{-16} cm^2 and that 10% of the dissociation leads to surface deposits.

The electrical conductivity, σ , of a material is related to its real and imaginary indices of refraction ($\hat{N} = N_1 - i N_2$) by $N_1^2 N_2 = 2 \pi \sigma / \omega$. From Reference 4, we find that $N_1 \approx 1.8$ and $N_2 \approx 0.5$ at $\lambda = 1 \text{ } \mu\text{m}$. This gives $\sigma \approx 5 \times 10^{14} \text{ s}^{-1} \approx 5 \times 10^4 \text{ mho/m}$. If we assume an accelerating gap voltage of 250 kV/m along the surface and a surface layer thickness of $3 \times 10^{-3} \text{ } \mu\text{m}$, this conductivity would lead to surface currents of 0.4 A per cm of width.

This amount by itself is probably negligible, but there could be a breakdown problem if the surface conductivity led to a redistribution and therefore to a concentration of field strength above breakdown levels, or if concentrated currents caused an explosive evaporation of the surface material at some points. Thus, decomposition of benzene with surface deposition of the heavy polymeric products could lead to accelerator problems after extended periods of use.

Note that the fragmentation caused by laser photodissociation will be in addition to the electron bombardment effects reported here.

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